



## Research Article

# Peculiarities of Calcite Interaction with Carboxylic Acids

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**Abstract:** This research examined the interaction of calcite with carboxylic acids (formic, citric, malic, and oxalic acids) at temperatures ranging from 22 to 80 °C. Experiments were carried out using an open batch reactor to prevent the impact of aggressive  $CO_2$  byproducts. The dissolution rate was determined to be a combination of the chemical interaction of calcite with acid and the promotion of dissolution by calcium carboxylate salt. When acid concentrations are low, the surface chemical reaction acts as a limiting step with an activation energy of 42 kJ·mol<sup>-1</sup>. Conversely, at higher acid concentrations, the formation of calcium carboxylate with reduced solubility hinders its dissolution, thereby restricting the overall calcite dissolution process. Both stages are significantly influenced by temperature. The specific functional groups present in the acids aid in the formation of surface species with  $Ca^{2+}$  cations. The properties of these functional groups impact the stability of the species and the dissolution of calcite.

**Keywords:** calcite, dissolution, carboxylic acids, mechanism, reaction order, limiting stage, activation energy

## 1. Introduction

Calcite has been widely applied in many fields of science and technology as a filler in polymers or pigment in paints<sup>1</sup> and as a catalyst or substrate in chemical engineering<sup>2</sup> and as a starting material for dissolution with carboxylic acids to remineralize desalinated water.<sup>3,4</sup> Carboxylic calcium salts are used in the food industry as acidity regulators, stabilizers, color fixators, food preservatives, flavoring agents and sources of digestible calcium.<sup>5-7</sup> Calcite precipitation from the aqueous phase containing some additives, such as carboxylic acids,<sup>8</sup> or calcite treatment with solutions of carboxylic acids<sup>9</sup> provides control over the particle size and morphology of the products. Acidizing treatment of a carbonated matrix results in additional porosity as well as channels in reservoirs.<sup>10</sup>

To design effective technologies, a fundamental understanding of the kinetics is needed. The calcite dissolution process has been studied in  $HCl$ <sup>11-16</sup> and  $CO_2$ -water systems.<sup>17,18</sup> The interest in organic acids is mainly limited to acetic acid.<sup>11,19-22</sup> Moreover, organic acids present numerous advantages compared to conventional mineral acids, including non-corrosive properties, safety, environmental sustainability, biodegradability, and ease of management. Solid crystalline acids are particularly advantageous for transportation and storage purposes.

The kinetic investigation of calcite dissolution, involving both mineral and organic acids, is usually conducted in a rotating disk reactor.<sup>12-16,19,22</sup> At regular intervals, samples of the solution are withdrawn to assess the concentration of  $Ca^{2+}$  cations. However, in a closed reactor, the  $CO_2$  byproduct interacts with calcite, leading to potential confusion in distinguishing between the dissolution of calcite by the acid being investigated and the influence of the byproduct on the

results.

Our primary emphasis lies in the interactions between calcite and a solution of carboxylic acid, with less attention being given to the byproduct. To mitigate the influence of the byproduct on calcite, we utilized an open batch reactor to facilitate the expulsion of gaseous byproducts. This methodology proves instrumental in enhancing our understanding of the chemical interplay among key reactants. A comprehensive grasp of the mechanism behind calcite dissolution opens avenues for the development of novel and enhanced applications of acids in geological and industrial contexts.

## 2. Experimental

### 2.1 Sampling

Pure analytical grade  $CaCO_3$  powder (Labtekh Co., Ltd.) was used as a reactant. The powder was shown to be pure calcite by X-ray analysis. The average particle size determined with a Partica LA-960 laser particle size (Horiba Ltd.) was 8.4  $\mu\text{m}$ . Cubes ( $2 \times 2$  cm) were cut from a marble slab (GeoStil Co., Ltd., 99% calcite, and quartz), and washed with 1%  $HCl$  for 30 s followed by rinsing with distilled water.

The solutions of reactants were prepared using distilled water and reagent-grade carboxylic acids, including formic acid (85%, Prime Chemicals Group Ltd.), oxalic acid (chemically pure grade, RM Engineering Ltd.), malic acid (99%, Prime Chemicals Group Ltd.), and citric acid (analytically pure grade, RM Engineering Ltd.). These chosen acids encompass a spectrum of carboxylic acid structures, ranging from simple monocarboxylic formic acid to the more intricate dicarboxylic oxalic and malic acids and tricarboxylic citric acid. Malic acid and citric acid are classified as hydroxy acids due to their possession of an additional electrophilic hydroxyl group, which influences acid adsorption. It is crucial to investigate the interactions of these acids with calcite at ambient and elevated temperatures up to 80 °C to assess their potential applicability in natural carbonate reservoirs and industrial settings.

### 2.2 Determination of the calcite dissolution rate

#### 2.2.1 $CaCO_3$ powder

The experimental runs at 22 °C were started by adding 0.75 g of calcite powder (AUW 320, Shimadzu; weight determination accuracy, 1 mg; scale division value, 0.1 mg) to 0.3 L of 5 mM acid reactant solution in a 1-L Pyrex flask with a magnetic armature followed by vigorous stirring at 1,000 rpm. The flask was hermetically sealed using a rubber stopper, and concurrently, a stopwatch and a magnetic stirrer (MR Hei-Tec, Heidolph) were used to activate the flask. The extent of  $CO_2$  gas release was measured using a burette. To examine the influence of temperature within the operational range of 22-80 °C, 0.60 g of  $CaCO_3$  powder was introduced into a 1-L Pyrex flask containing 0.3 L of 20 mM formic acid at the specified temperature.

The acid conversion was determined by evaluating the proportion of the released  $CO_2$  gas amount (mol) to the initially loaded acid quantity (mol), considering the stoichiometric ratio of the carboxylic group components to calcium as 2:1. The reaction order and rate constant were determined by studying the dependence of acid concentration,  $C$ , on time,  $\tau$ , as well as on the half-conversion time (50% acid conversion),  $\tau_{1/2}$ , by means of formal kinetics.

#### 2.2.2 Marble cubes

A marble cube ( $2 \times 2$  cm) was lowered into a Teflon cup loaded with 60 ml of 0.25 or 0.5 M acid, covered with a lid allowing free gas to reach the outlet, and placed on the platform of an analytical balance (AUW 320, Shimadzu; weight determination accuracy, 1 mg; scale division value, 0.1 mg). The temperature was maintained at 22 °C. The acid conversion and the half-conversion times were determined as above.

To study the effect of temperature on the reaction rate, a series of marble cubes was dissolved at 80 °C in 60 ml of 0.5 M acid (in an oven) for 5-120 min. The amount of dissolved calcite was evaluated as the difference in cube weight before and after the experimental procedure.

### 2.2.3 Computations

The calcite dissolution rate ( $W$ , mol·min.<sup>-1</sup>·m<sup>-2</sup>) was calculated from changes in the amount of CO<sub>2</sub> gas released over time. The kinetic parameters were determined by means of formal kinetics.<sup>23</sup> The reaction order on acid ( $n$ ) was estimated from the relationship between the half-conversion time ( $\tau_{1/2}$ ) and the constant rate ( $k$ ) (1)-(3):

$$\tau_{1/2} = \frac{C_o}{2k} \text{ for } n = 0 \quad (1)$$

$$\tau_{1/2} = \frac{0.693}{k} \text{ for } n = 1 \quad (2)$$

$$\tau_{1/2} = \frac{1}{kC_o} \text{ for } n = 2 \quad (3)$$

where  $C_o$  is the initial concentration of the acid. The half-conversion times were determined from kinetic curves produced for calcite dissolution in 0.25 and 0.5 M acids. The reaction order on acid was accepted when the acid concentration had no effect on the reaction constant calculated with equations (1)-(3). The apparent activation energy ( $E_a$ ) for the dissolution reaction was determined from the Arrhenius equation (4):

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (4)$$

where  $R$  is the universal gas constant,  $T$  is the absolute temperature and  $A$  is the preexponential factor.

## 3. Results and discussion

### 3.1 Theoretical background

A basic concept in chemical kinetics is that heterogeneous processes consist of a series of physical and chemical stages. For solid dissolution in liquid, these stages include (a) convection of reactants through solution to the solid surface, (b) adsorption of the reactants onto the solid surface, and (c) chemical reactions between the adsorbed reactant and solid, which may, in turn, consist of several intermediate steps, including bond breakage and formation, (d) diffusion of the products through the boundary layer, and (e) desorption of the products away from the surface to the bulk solution. One of the stages will be the slowest and limit the process overall. Stages (a), (b), (d) and (e) involve the physical transport of reactants and products through the solution to and from the surface. Stage (c) occurs on the solid surface and consists of electron interactions; this stage has a chemical nature and an activation energy of at least 40 kJ·mol<sup>-1</sup>. Kinetic parameters (reaction order on acid, rate constant and temperature dependence) may be used to gain insight into the dissolution mechanism.

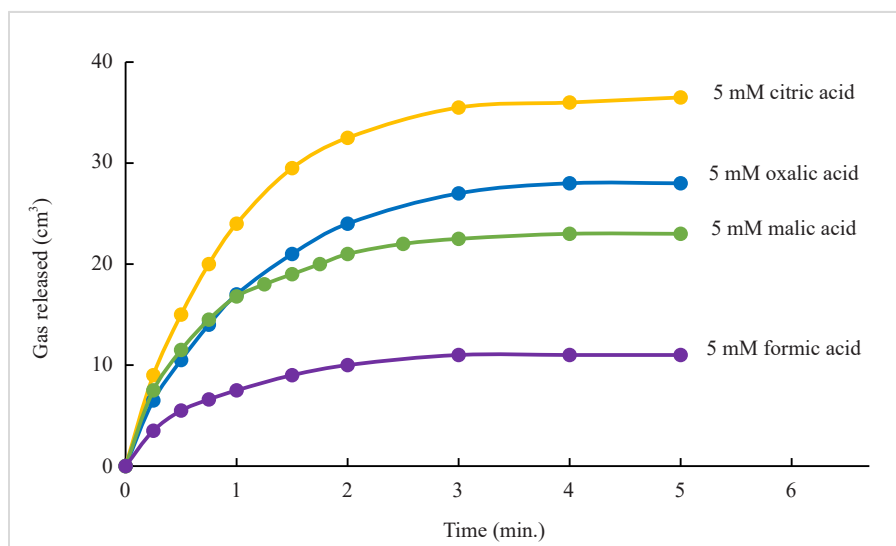
### 3.2 Acid concentration

The coexistence of multiple stages proceeding simultaneously greatly complicates understanding and quantification. It is desirable, therefore, to select a stage and examine one at a time. One of the most important stages is chemical interaction. To slow the latter, it is necessary to reduce the chemical reaction rate. In accordance with the Arrhenius equation:

$$W = kC^n S \quad (5)$$

where  $C$  is the reactant concentration,  $n$  is the reaction order on acid, and  $S$  is the solid surface area. A lower reactant concentration  $C$  is associated with a lower surface reaction rate  $W$ . Therefore, we used diluted 5 mM acid solutions to dilute the chemical surface reaction to the limiting stage.

Figure 1 shows the  $CO_2$  gas evolution during calcite dissolution in diluted 5 mM acids. The acid activity increased from formic to citric acid according to the order of formic  $\ll$  malic~oxalic  $<$  citric acid. A previous study<sup>24</sup> revealed the rate constant dependence on acid features (acidity constant index, number of carboxylic groups, and influence of other functional groups).



**Figure 1.** Plots of  $CO_2$  gas evolution vs. time for  $CaCO_3$  powder dissolution in 5 mM carboxylic acids at 22 °C

Figure 2 shows the results of marble cube dissolution for more concentrated 0.5 M carboxylic acids. In contrast, as shown in Figure 1, 0.5 M formic acid exhibited the highest activity, whereas oxalic acid was not active. The 0.5 M acid activity range was oxalic~tartaric  $\ll$  citric  $<$  malic  $<$  formic. However, at a lower acid concentration (0.25 M), the activity trend changed to formic acid  $<$  malic acid  $<$  citric acid (Figure 2), which is similar to that for diluted 5 mM acids (Figure 1).

Analysis of the kinetic curves of the 0.25 and 0.5 M solutions with formal kinetic equations (1)-(3) revealed that the reaction rate order was 2 for formic acid and 1 for malic acid, aligning with findings reported by Compton et al.,<sup>25</sup> and 0 for citric acid (Table 1).

It is noteworthy that the reaction rate order is related to the mechanism. If acid adsorption is the limiting stage



and the process rate ( $W$ ) is given by

$$W = k_{ads}C \quad (7)$$

where  $k_{ads}$  is the adsorption rate constant and  $C$  is the concentration of acid. The reaction rate order with respect to the acid is 1.

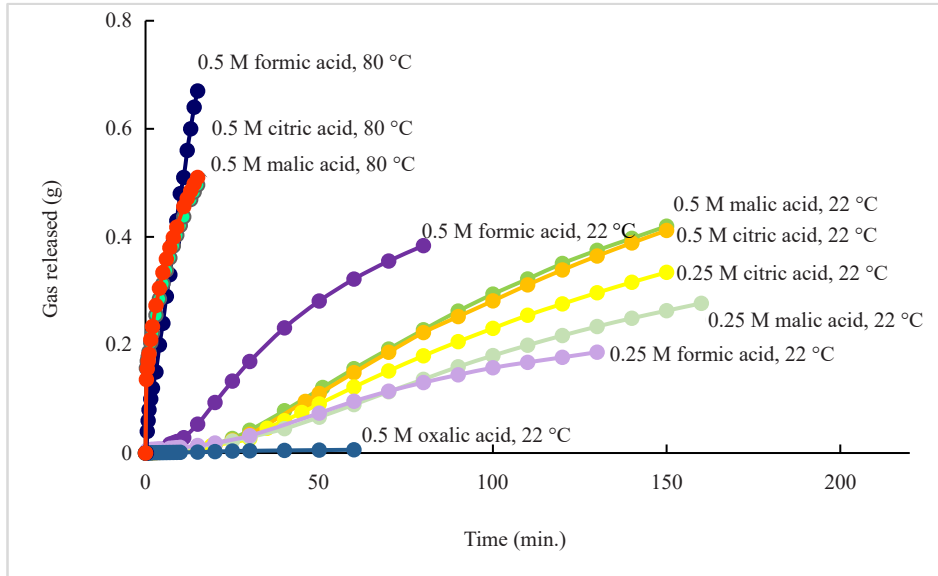
When the bimolecular chemical reaction of divalent  $Ca(II)$  with two carboxylic groups



is the limiting stage then, the process rate ( $W$ ) is limited by the surface chemical reaction

$$W = kC^2, \quad (8)$$

and the rate order on acid is 2.



**Figure 2.** Plots of gas evolution vs. time for marble cube ( $2 \times 2$  cm) dissolution in carboxylic acids

**Table 1.** Evaluation of the reaction rate order on acid (for the 1st  $-COOH$  group) for the dissolution of calcite in formic, malic and citric acids at 22 °C

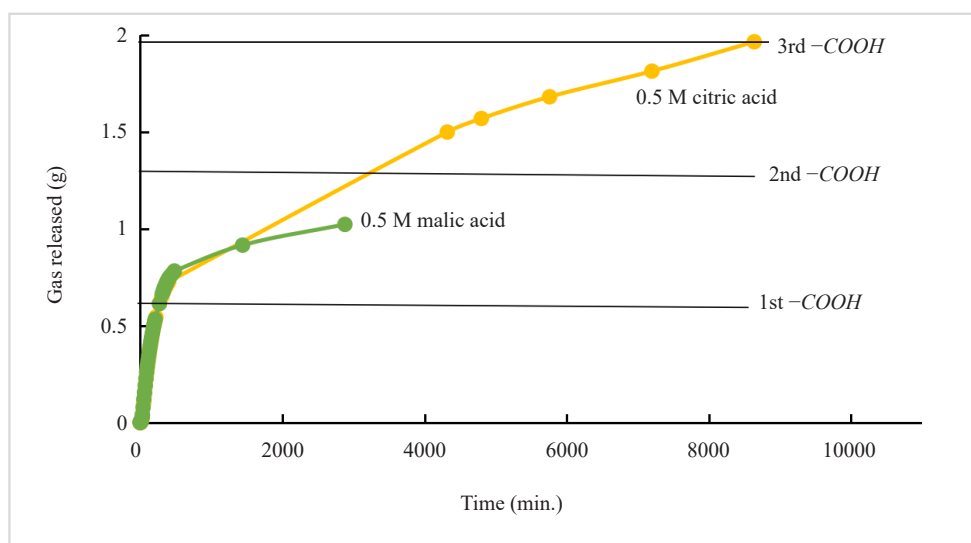
Parameter	$C_o$	$\tau_{1/2}$	$k = \frac{0.69}{\tau_{1/2}}$	$k = \frac{1}{\tau_{1/2}C_o}$	$k = \frac{C_o}{2\tau_{1/2}}$
	[M]	[min.]	(1st order)	(2nd order)	(0th order)
Formic acid	0.5	62	0.0111	<u>0.032</u>	0.0040
Formic acid	0.25	106	0.0065	<u>0.037</u>	0.0012
Malic acid	0.5	94	<u>0.0073</u>	0.021	0.0027
Malic acid	0.25	92	<u>0.0075</u>	0.044	0.0014
Citric acid	0.5	127	0.0059	0.017	<u>0.0021</u>
Citric acid	0.25	69	0.0093	0.054	<u>0.0017</u>

If the diffusion and transport of products limit the process overall, then the dissolution rate is not affected by the acid concentration, and the reaction rate order on the acid is 0.

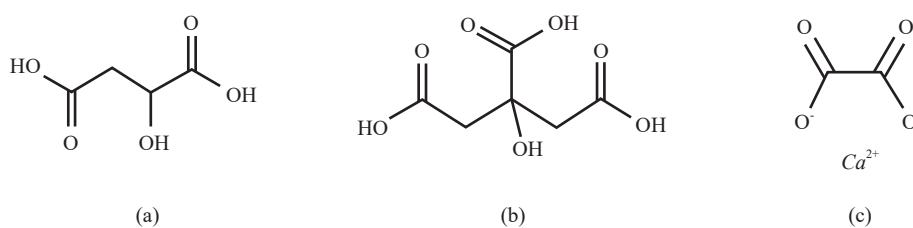
With the above, the limiting stage of the 2nd order reaction of calcite dissolution in formic acid is the surface

chemical reaction. The 0-order reaction of calcite with citric acid is controlled by product diffusion. According to reference data,<sup>26</sup> calcium citrate has a much lower solubility in water (0.095 g/100 mL) than calcium formate (18 g/100 mL). The dissolution rate of calcium citrate is likely rather slow and limits the process of calcite dissolution in citric acid. The 1st order for malic acid is evidently associated with the interplay between the 2nd order surface chemical reaction and the 0th order product dissolution, both of which progress at comparable rates rather than acid adsorption.

The experimental findings demonstrated that polycarboxylic hydroxy acids exhibit a stepwise reaction mechanism (Figure 3). The 1st carboxylic group in both malic and citric acids displayed considerably greater reactivity in calcite dissolution than did the 2nd and 3rd carboxylic groups. Importantly, the 1st carboxylic group is linked with the hydroxyl OH group via the C atom (Figure 4 (a, b)), making it the most potent carboxylic group (Table 2). The less acidic 2nd and 3rd carboxylic groups are linked with the hydroxyl OH group via two C atoms of the carbon chain (Figure 4 (a, b)). Considering the molecular structure of carboxylic hydroxy acids (Figure 4 (a, b)), characterized by a C-C bond length of 0.154 nm for the carbon chain, C-O distances of 0.143 and 0.137 nm for the hydroxyl group and the carboxylic group, respectively, and the tetrahedral structure of the hydrocarbon chain's carbon atoms due to its  $sp^3$  hybridization with bond angles of approximately  $109^\circ$  between its four  $\sigma$ -bonds, it can be inferred that the distance between the hydroxyl group and the 2nd or 3rd carboxylic group aligns with that between two adjacent  $Ca^{2+}$  cations in calcite (0.4724 nm<sup>27</sup>). This suggests the potential for the acid anion to bind to the calcite surface via bridge-like bonding between the mentioned groups and the  $Ca^{2+}$  cations. When the 2nd or 3rd carboxylic group adsorbs on the surface  $Ca^{2+}$  cation, the oxygen atom of the hydroxyl group donates its unshared electron pair to the vacant shell of the adjacent  $Ca^{2+}$  cation, resulting in the formation of a bridge-like surface species, as opposed to the dianion adsorption proposed by Compton et al.<sup>25</sup>



**Figure 3.** Plots of  $CO_2$  gas evolution vs. time for marble cube ( $2 \times 2$  cm) dissolution in 0.5 M citric and malic acids at 22 °C



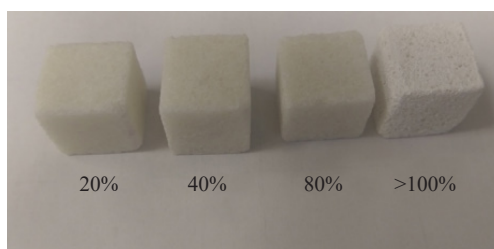
**Figure 4.** Structures of malic (a) and citric (b) acids and calcium oxalate (c)

**Table 2.** Characteristics of carboxylic acids

Parameter	$pK_a$ of acid			pH of 0.5 M acid solution		
	$pK_{a1}$	$pK_{a2}$	$pK_{a3}$	pH <sub>1</sub>	pH <sub>2</sub>	pH <sub>3</sub>
Formic acid	3.75	-	-	2.02	-	-
Malic acid	3.46	5.05	-	1.88	2.68	-
Citric acid	3.13	4.76	6.39	1.71	2.53	3.35
Oxalic acid	1.25	4.14	-	0.78	2.22	-

The bridge-like surface species are likely to possess notable stability, as evidenced by the significant decrease in calcite dissolution with the increase in the activity of the 2nd and subsequently the 3rd carboxylic groups (Figure 3). Visual observation additionally revealed the formation of surface sediment following the addition of the 2nd carboxylic group of citric acid (Figure 5).

Owing to the relatively close proximity between the two carboxylic groups in oxalic acid, they can adsorb onto the same  $Ca^{2+}$  cation (Figure 4 (c)). This structural configuration exhibited significant stability in solution, effectively impeding calcite dissolution at both room temperature and 80 °C. This phenomenon is ascribed to the robust ionic bonds formed between the carboxylic groups and the calcium cation, facilitating the attachment of the organic anion to the calcite surface.

**Figure 5.** Photos of marble cubes (2 × 2 cm) after the 1st  $-COOH$  group of citric acid was converted to 20, 40, 80 and >100%

### 3.3 Temperature effect

#### 3.3.1 Activation energy

The effect of temperature on the rate of the chemical stage was studied for the 2-d order reaction of calcite dissolution in 0.02 M formic acid by the Arrhenius dependence (4). The reaction rate constant ( $k$ ) was evaluated from the plot of  $1/C$  vs. time (Figure 6). The dependences produced are fitted by the following expressions (9)-(14):

$$22\text{ }^{\circ}\text{C}: y = 1.77x + 53.3; R^2 = 0.981 \quad (9)$$

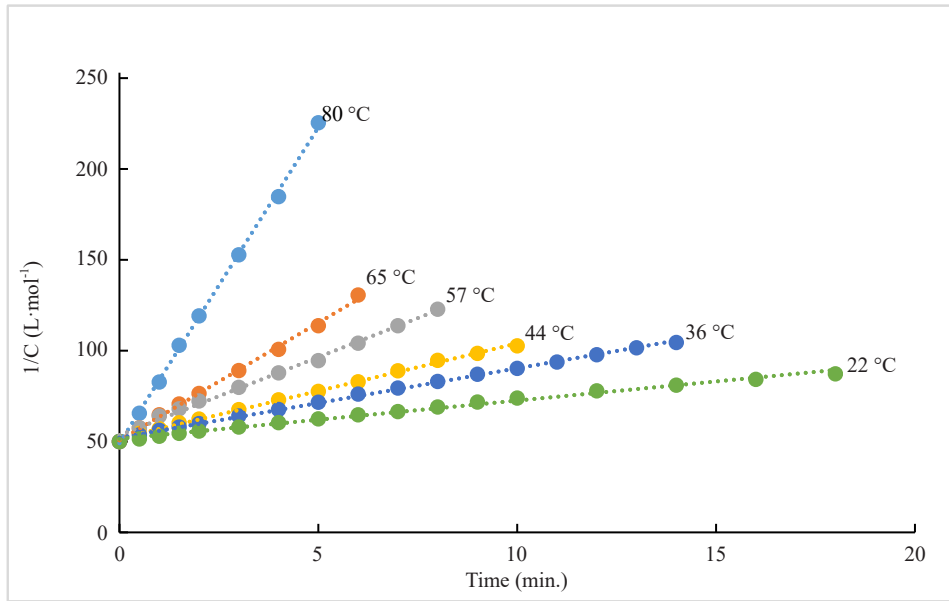
$$36\text{ }^{\circ}\text{C}: y = 3.82x + 52.1; R^2 = 0.998 \quad (10)$$

$$44\text{ }^{\circ}\text{C}: y = 5.23x + 51.7; R^2 = 0.998 \quad (11)$$

$$57\text{ }^{\circ}\text{C}: y = 8.59x + 53.5; R^2 = 0.995 \quad (12)$$

$$65\text{ }^{\circ}\text{C}: y = 12.9x + 50.6; R^2 = 0.998 \quad (13)$$

$$80\text{ }^{\circ}\text{C}: y = 34.8x + 49.1; R^2 = 0.999 \quad (14)$$

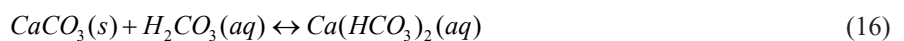


**Figure 6.** Plot of the reverse concentration of formic acid in contact with a marble cube ( $2 \times 2$  cm) at 22-80 °C vs. time

The temperature dependence of the rate reaction constant  $k$  (Figure 7) is described by expression (15):

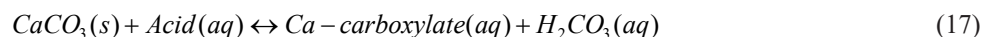
$$\ln k = 18 - \frac{5.1 \times 10^{-3}}{T}, R^2 = 0.98 \quad (15)$$

yielded a value for  $E_a/R$  of  $5.1 \times 10^{-3}$  which corresponds to an activation energy of  $42 \text{ kJ} \cdot \text{mol}^{-1}$ . An identical value was obtained through calculations involving half-time conversion. This value is similar to that reported for calcite dissolution in carbonic acid at 5-48 °C ( $10 \text{ kcal} \cdot \text{mol}^{-1}$ ) by Compton et al.<sup>25</sup> via the channel flow cell technique and indicates that the calcite dissolution process is controlled by the surface chemical reaction stage. These findings contrast with those documented by Fredd and Fogler,<sup>19</sup> who determined an activation energy of  $25.1 \text{ kJ} \cdot \text{mol}^{-1}$  for the dissolution of calcite in acetic acid up to 50 °C, and by Buijse et al.,<sup>22</sup> who identified an activation energy of  $13 \text{ kJ} \cdot \text{mol}^{-1}$  for carbonate dissolution in acetic and formic acids up to 80 °C utilizing a rotating disk apparatus. The reduced activation energy values are probably a result of constraints imposed by the physical transport stage<sup>19</sup> and are not appropriate for making definitive conclusions regarding the particular attributes of surface chemical interactions. Within a sealed reactor, the presence of carbonic acid,  $H_2CO_3$ , generated upon  $CO_2$  dissolution in water influences the calcite dissolution process through two competing reactions. Calcite dissolution occurs via carbonic acid as a result of the creation of the significantly soluble calcium bicarbonate (16):



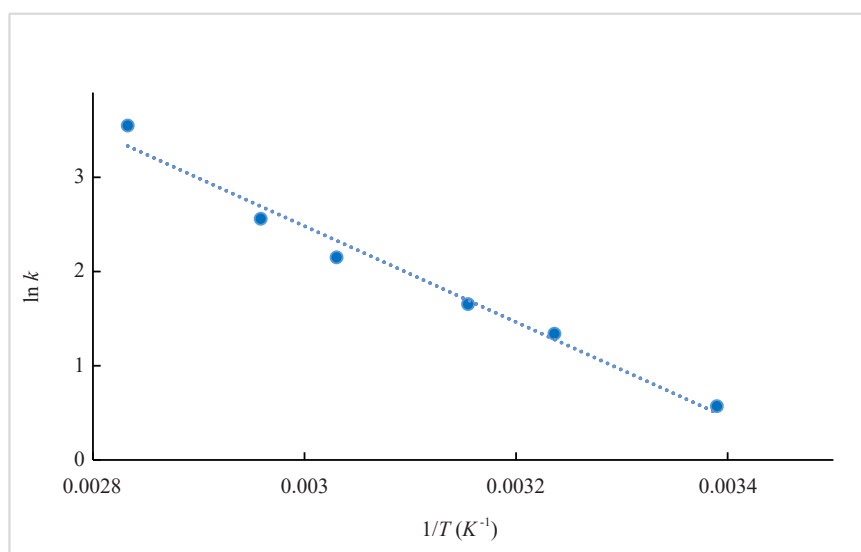
The carboxylate salt produced also reacts with carbonic acid, shifting the reaction equilibrium toward the reactants (17):





Our results showed that removing the byproduct from the reaction mixture allowed us to explore the chemical effect of the acid under study. By removing the byproduct from the reaction mixture, we can eliminate these potential interferences and focus on the chemical effect of the acid itself. This allows us to more accurately study the reactivity of the acid, its reaction mechanisms, and its overall effect on the reaction.

Our findings indicate that the removal of the byproduct from the reaction mixture enables an in-depth investigation into the chemical impact of the acid under examination. As a result, we can mitigate these potential interferences and concentrate on the intrinsic chemical influence of the acid. This approach facilitates a more precise examination of the reactivity of the acid, its reaction mechanisms, and its comprehensive impact on the reaction.



**Figure 7.** Plot of the rate constant of the surface reaction of calcite with formic acid vs. the reverse temperature

### 3.3.2 Solubility

Temperature is known to affect the rates of both surface chemical reactions (the chemical stage of the process under consideration) and the solubility of the surface species generated (the physical stage). Elevating the temperature to 80 °C resulted in an increase in gas emission from a reactor containing a marble cube and formic acid (Figure 2). The activity of the 1st carboxylic group of hydroxy acids at 80 °C was notably elevated (Figure 2), in contrast to that of oxalic acid.

Experimental runs conducted in an oven revealed that malic acid was entirely consumed at 80 °C within 30 minutes, which was attributed not only to the relatively high activity of the 2nd carboxylic group but also to the solubility of the surface species that formed. Marble cube exposure to citric acid at 80 °C resulted in the formation of surface deposits within 30 minutes. These findings align with those of Apelblat,<sup>28</sup> indicating that an increase in temperature enhances the solubility of calcium malate while diminishing that of calcium citrate.

## 4. Conclusion

In this investigation, an open batch reactor was used to examine the kinetics of the interaction between calcite and carboxylic acid. The rate of the surface chemical reaction was relatively low, and the generation of gas bubbles

facilitated the acceleration of reactant and product convection within the solution. This approach enabled the circumvention of physical transport constraints, leading to precise kinetic data acquisition.

The dissolution of calcite into carboxylic acids entails a multifaceted process encompassing both chemical and physical stages. The predominant mechanism is contingent upon the concentration of the acid solution and the temperature. The dissolution of calcite into carboxylic acids is impeded by a decrease in the chemical or physical stage. For low-concentration acid solutions, the chemical stage emerges as the constraining factor, while higher acid concentrations prompt the physical stage to assume this role. By enhancing the solubility of the surface species, it becomes feasible to surmount the limiting influence of the physical stage and enhance the overall rate of calcite dissolution.

Furthermore, the configuration of the carboxylic acid molecule plays a pivotal role in the stability of the surface species. Carboxylic acids with few functional electrophilic groups (such as carboxylic and carboxyl groups) and a structure conducive to bridge-like adsorption on the calcite surface engender surface species with varying stabilities. The most steadfast surface species impeding calcite dissolution are generated by the strong ionic bonds between two carboxylic groups (e.g., oxalic acid) and the same surface  $Ca^{2+}$  cation. Conversely, the bridge-like complex between two  $Ca^{2+}$  cations formed through the ionic bond of a hydroxyl group and the coordination bond of a carboxylic group (e.g., malic and citric acids) exhibits decreased stability.

This study provides valuable insights into the mechanism and kinetics of calcite interactions with carboxylic acids. The outcomes of this research can guide the selection of appropriate acids and conditions to optimize the efficacy of calcite across a spectrum of applications, ranging from surface modification to matrix dissolution.

## Compliance with ethical standards

This article does not contain any studies with human or animal subjects.

## Conflict of interest

The authors declare no competing financial interest.

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